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Ring opening metathesis polymerisations of norbornene and norbornadiene derivatives containing oxygen: a study on the regeneration of Grubbs catalyst

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Abstract—Ring opening metathesis polymerisation (ROMP) of norbornene and norbornadiene derivatives containing oxygen are investigated using Grubbs well-defined ruthenium initiator. A series of 7-alkoxy norbornadiene monomers (**2b**–**d**), containing alkoxy groups with decreasing steric hindrance in the 7-position have been prepared. The ROMP reactions of monomers showed that as the reaction proceeds the initiator is consumed first and then is partially regenerated at the expense of the propagating species. A small amount of another carbene species X, giving a broad signal at 17.44 ppm, is also formed which is extremely stable in solution. The species X is an active metathesis species and is able to perform ROMP on strained cyclic olefins. ROMP of monomers without alkoxy groups in the 7-position (**3**, **4a**, **4b**, **5a** and **5b**) and also monomers with alkoxy groups in the 5 and/or 6 positions of norbornene (**6** and **7**) have been performed under similar conditions. None of these systems exhibited regeneration of the initiator and no resonances due to species X can be seen in the ^{1}H NMR spectra. The results confirm that the presence of oxygen in the 7-position of the norbornadiene monomer plays an important role in the process of regeneration of the initiator. It is found that the steric bulk and the position of substituents of the monomer have a pronounced influence on the extent of regeneration of the initiator.

1. Introduction

The olefin metathesis reaction has become an invaluable synthetic tool for chemists. The ability to simultaneously cleave and reform carbon–carbon double bonds has led to its widespread use in the design of useful organic molecules[1] and polymers.[2]

Although olefin metathesis was discovered as early as 1955,[3] it has only achieved a leading role in synthetic methodology in the last decade. This is mainly attributed to advances in the field of catalysis and organometallic chemistry, which have been heavily influenced by the work of Grubbs[4–6] and Schrock[7] in developing well-defined transition metal carbene complexes. This new generation of catalysts are powerful tools in the field of organic reactions[1] such as ring opening metathesis (ROM), ring closing metathesis (RCM)[8] and cross metathesis (CM), and in polymerisation reactions such as ring opening metathesis polymerisations (ROMP)[2] and acyclic diene metathesis (ADMET).[9] They have also found many applications in the synthesis of natural products.[10–12]

Schrock introduced well-defined molybdenum initiators with bulky alkoxide and arylimido ligands of the type $Mo(CHR)(NAr)(OR')_2$ [R=$-CMe_3$ and R′=$-CMe_3$ or $-C(CF_3)_2Me$] which allowed a high degree of control of molecular weight, polydispersity, *cis*/*trans* content and, in favourable cases, tacticity.[13–16] The key to controlled polymerisation is that while the molybdenum initiators are inactive towards double bonds in the polymer chain, they react rapidly with the strained double bonds in the monomer to give a linear polymer. However, these catalysts are limited by the high oxophilicity of the metal centres, which renders them extremely sensitive to oxygen and moisture. As a result of this, they show limited tolerance towards functional groups, reducing the number of potential monomers.

The key to improved functional group tolerance was the development of catalysts that react preferentially with olefins in the presence of heteroatoms. Grubbs et al.[6] synthesised ruthenium alkylidene complexes of the type $RuCl_2(PCy_3)_2(=CHPh)$ [**1**], which are tolerant to a wide range of functional groups such as acids, alcohols,

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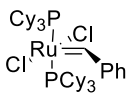

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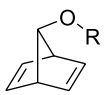

2a:R=C(CH$_3$)$_3$
2b:R=CH(CH$_3$)$_2$
2c: R=CH$_2$CH$_3$
2d:R=CH$_3$

Figure 1. Grubbs ruthenium benzylidene initiator and 7-alkoxy norbornadienes.

aldehydes, esters and amides.[6] Kinetic studies on these catalysts revealed that catalyst **1** is an efficient initiator for the ROMP of strained cyclic olefins, permitting the incorporation of high degrees of functionality into the resulting polymers.

ROMP reactions using well-defined initiators result in polymers with a narrow polydispersity index (PDI~1.05–1.2). Generally, the initiator is totally consumed and the disappearance of the initiator alkylidene proton and the appearance of the propagating alkylidene protons can be seen in ^{1}H NMR spectra. In this paper we report the ROMP of 7-alkoxynorbornadienes, in which the initiator is first consumed and then regenerated at the expense of the living propagating species.

2. Results and discussions

We recently made a remarkable observation when catalyst **1** was used to initiate the polymerisation of 7-*t*-butoxynorbornadiene **2a** (Fig. 1) using a monomer–initiator ratio ($[M]_o/[I]_o$) of 50.[17] The reaction proceeds rapidly in $CDCl_3$ with almost complete consumption of initiator to form propagating ruthenium alkylidene species which are then converted slowly, but not completely, back to initiator, implying a secondary metathesis reaction. The stack plot of the alkylidene proton region at intervals over a 12 h period for this ROMP reaction, Fig. 2, shows these extraordinary features, and it clearly exhibits the presence of three distinct signals. Resonances due to alkylidene protons of **1** appear at 19.9 ppm, a propagating species (P_n) has signals at 19.38, 19.36, 19.33 ppm, and a species X appears at 17.44 ppm. The three propagating signals (P_n) are believed to arise due to the sensitivity of the chemical shift to the *cis*/*trans* isomerism of the adjacent double bond and to the *meso*/*racemic* isomerism of the adjacent dyad.[18] The initiator is visibly regenerated at the expense of the propagating species as the reaction proceeds. This can only occur by a secondary metathesis reaction by either an intra- or intermolecular reaction at the living chain ends of the propagating species, Fig. 3. In the intramolecular reactions, (Fig. 3, route a), the end groups of a chain react to form a macrocycle, regenerating the initiator. Whereas, in the intermolecular reactions, (Fig. 3, route b), the end groups from two chains react, resulting in regeneration of the initiator and a new propagating species, which has a combined molecular weight of the original propagating chains. GPC measurements have previously been carried out to investigate this process and unambiguously demonstrate that one or both of these secondary metathesis reactions must take place.[18] Another consequence of these intra and/or intermolecular reactions is a decrease in the proportion of end groups in the polymer. As expected, analysis of the resulting polymers using ^{13}C NMR revealed that polymer terminated with ethyl vinyl ether after 24 h had fewer vinylic end groups than that of polymer terminated in the same manner immediately after all of the monomer had been consumed.[18] A small amount of another carbene species, labelled X, giving a broad signal at 17.44 ppm, (Fig. 2), is also formed which is extremely stable in solution. This observation of regeneration of the initiator during a ROMP reaction was the first of its kind and it has not been observed in any other systems. In particular, it has not been observed in the ROMP of 7-alkyl derivatives of norbornadiene.

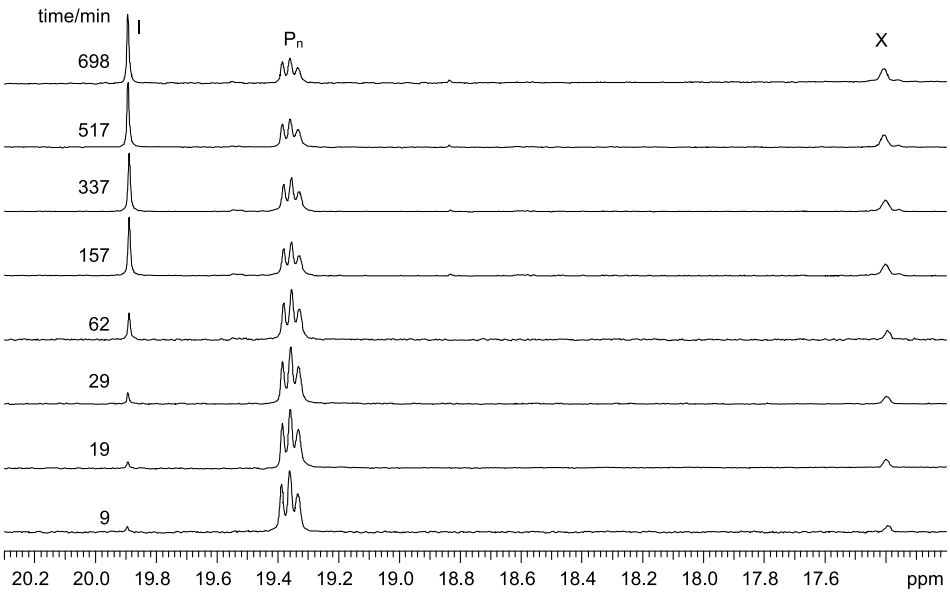

Figure 2. Stack plot showing the alkylidene region of the ^{1}H NMR spectra for the first 12 h of the ROMP reaction of **2a** initiated by **1** in $CDCl_3$ system ($[M]_o/[I]_o$=50).

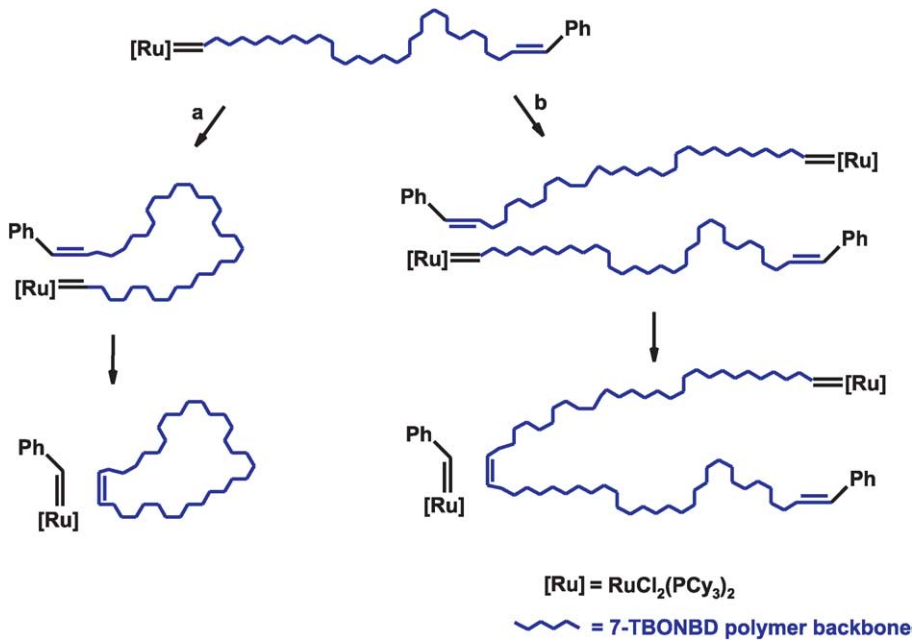

Figure 3. Schematic showing that secondary metathesis leads to regeneration of the initiator by (a) intramolecular cyclisation, or (b) intermolecular reactions.

2.1. The effect of the nature of the substituents on the regeneration of the initiator

In an attempt to probe the parameters which govern the process of regeneration of the initiator, we have investigated whether regeneration is apparent in any other ROMP systems mediated by initiator **1**. Polymerisations of norbornene and the oxygen-containing norbornene derivatives **3**, **4a**, **4b**, **5a** and **5b**, shown in Figure 4, have been performed under similar conditions to those described for the ROMP of **2a** initiated by **1**, and the results are shown in Table 1. The reactions were followed by ^{1}H NMR and, although they behaved differently in terms of the rate of monomer consumption and the amount of initiator consumed, none of these systems exhibited regeneration of the initiator. The alkylidene region (21–16 ppm) of the ^{1}H NMR spectra when monomers **3**, **4a**, **4b**, **5a** and **5b** are subjected to ROMP by **1** are shown in Figure 5, and it is clear that no resonances due to species X (~17.5 ppm) can be seen during the polymerisation of any of these monomers.

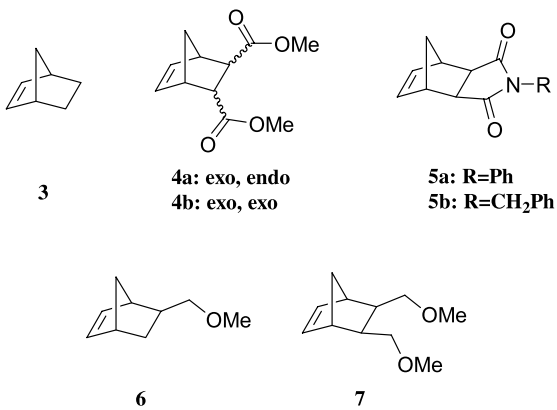

Figure 4. Various strained bicyclic monomers.

Table 1. ROMP of monomers **3**, **4a**, **4b**, **5a**, **5b**[a]

Monomer	Monomer consumption (h)	Initiator consumption (%)
3	<0.3[b]	34
4a	14	83
4b	1	95
5a	0.8	69
5b	<0.3[b]	91

[a] Polymerisations were performed in $CDCl_3$ at ambient temperature and were initiated by **1** using a ratio of $[M]_o/[I]_o$=50. $[I]_o$=15 mM. The reactions were followed by ^{1}H NMR spectroscopy. None of the reactions exhibited regeneration of the initiator.

[b] The monomer is completely consumed before the first ^{1}H NMR of reaction mixture is taken.

2.2. The effect of the steric bulk of alkoxy substituents in the 7-position of norbornadiene monomers on the process of regeneration of the initiator

The results discussed above suggest that the presence of oxygen in the 7-position of the norbornadiene monomer plays an important role in the process of regeneration for the ROMP of **2a** using initiator **1**. To investigate this effect, a series of new monomers, **2b**–**d** (Fig. 1), containing alkoxy groups with decreasing steric hindrance in the 7-position have been prepared. The ROMP reactions of monomers **2a**–**d** initiated by **1** in $CDCl_3$ were monitored by ^{1}H NMR spectroscopy. A spectrum was recorded every 15 min for the first 3 h and then at appropriate periods until it was clear that no further reaction was taking place. The alkylidene region (21–16 ppm) of these spectra are shown in Figure 6 and they all exhibit a resonance for the residual initiator (I), the propagating species (P_n) and the stable species X at 19.98, 19.50–18.50, and 17.5 ppm, respectively. Regeneration of the initiator is observed in all of these ROMP reactions, Table 2, and the extent of regeneration is found to increase as the steric bulk of the substituent in the 7-position increases. The regeneration of the initiator is believed to be facilitated by the co-ordination of oxygen from the propagating polymer backbone to the active ruthenium

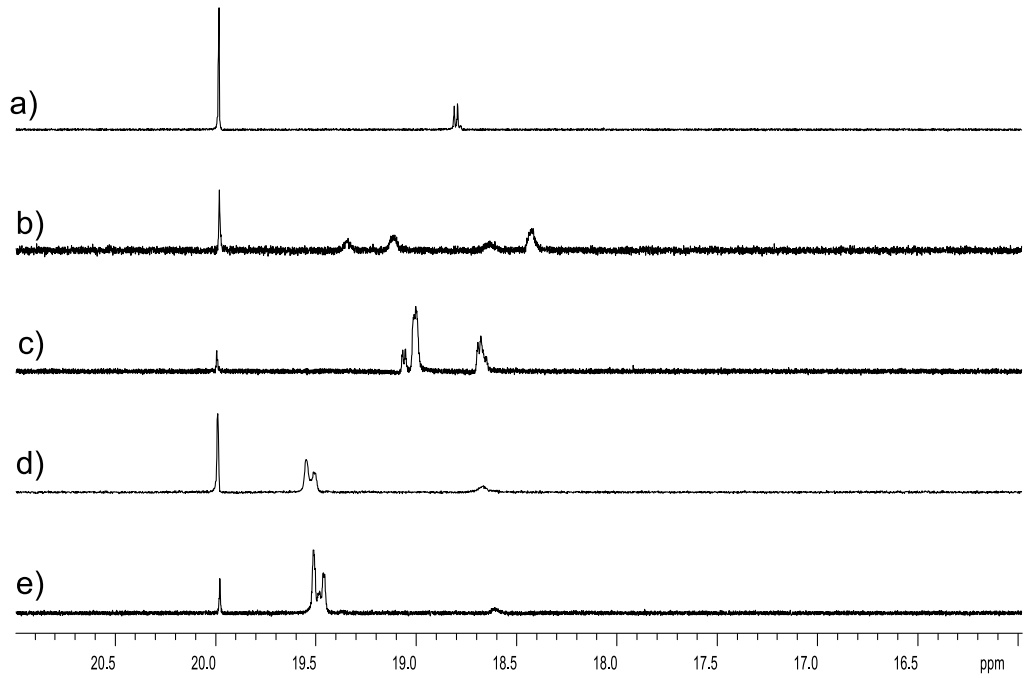

Figure 5. The alkylidene region (21–16 ppm) of the ^{1}H NMR spectra when monomers (a) **3**, (b) **4a**, (c) **4b**, (d) **5a** and (e) **5b** are subjected to ROMP by **1** using a ratio of $[M]_o/[I]_o=50$, $[I]_o=15$ mM at ambient temperature.

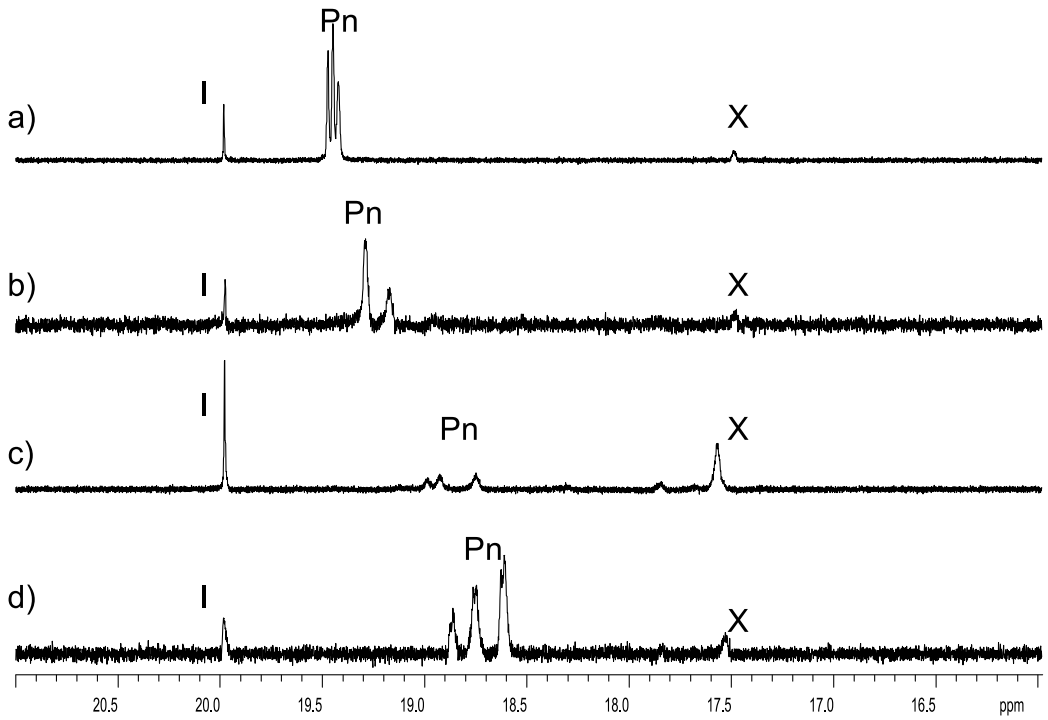

Figure 6. The alkylidene region (21–16 ppm) of the ^{1}H NMR spectra when monomers (a) **2a**, (b) **2b**, (c) **2c** and (d) **2d** are subjected to ROMP by **1** using a ratio of $[M]_o/[I]_o=50$, $[I]_o=15$ mM at ambient temperature.

metal centre.[18] If the chelating oxygen atom is at the chain end of either the same (Fig. 7, route a) or a different propagating species (Fig. 7, route b), then the terminal double bond is brought into close proximity with the ruthenium carbene and a subsequent secondary metathesis reaction may result in the formation of macrocycles or a polymer of increased molecular weight and regeneration of the initiator. At the moment our hypothesis is that the presence of bulky alkyl groups in the alkoxy substituent in the 7-position of the monomer makes the oxygen atom more electron rich, and hence a better electron donating moiety.[19]

As shown in Table 2, the polymerisation reactions of monomers **2a**–**d** initiated by **1** also provide information on how the steric bulk of the substituent in the 7-position of the norbornadiene unit affects other aspects of the polymerisation process such as the rate of monomer consumption and the consumption of initiator at the start of the reaction.

Table 2. ROMP of monomers **2a–d**[a]

Monomer	$[M]_o/[I]_o$	Monomer consumption (h)	Initial consumption of initiator[b] (%)	Extent of regeneration[c] (%)
2a	50	1	99	29
2a	25	0.5	93	27
2a	10	0.25	81	23
2b	50	2	98	15
2b	25	1	92	18
2b	10	0.5	75	13
2c	50	5	98	6
2c	25	3	92	8
2c	10	0.75	71	10
2d	50	5.5	97	8
2d	25	1	88	3
2d	10	0.5	65	1

[a] Polymerisations were performed in $CDCl_3$ at ambient temperature and were initiated by **1** with $[I]_o$=15 mM.
[b] Based on the ^{1}H NMR spectrum recorded after 15 min of reaction.
[c] The error associated with the extent of regeneration of the initiator is estimated to be ±5% of the quoted value. The reactions were followed by ^{1}H NMR spectroscopy.

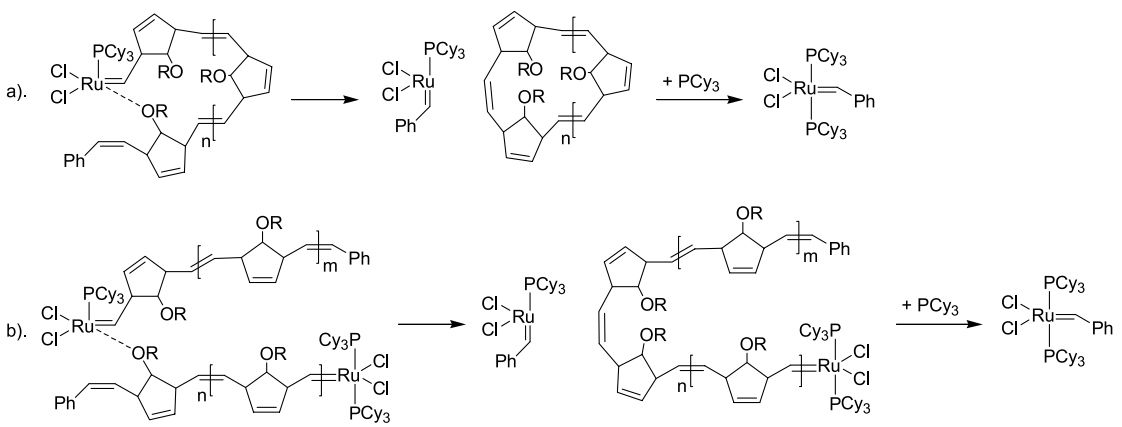

Figure 7. A schematic showing that secondary metathesis reactions at the propagating chain ends can result in regeneration of the initiator. This can be enhanced by (a) intra-, or (b) intermolecular chelation of an oxygen atom from the propagating chain end to the ruthenium metal centre. Species X does not figure in this scheme.

It is now well established that one of the phosphine ligands must dissociate from the ruthenium metal centre if initiation and propagation are to occur in ROMP reactions mediated by Grubbs catalyst.[20] This dissociation makes the metal carbene bond accessible for olefins to undergo the necessary [2+2]cyclo-addition reaction. The inserted monomer unit is in close proximity to the active ruthenium carbene centre, and its steric bulk can have a pronounced influence on the ability of the free PCy_3 ligand to re-associate to the metal centre. One possibility is that an increase in the steric bulk in the 7-position of the most recently inserted monomer unit will impede the re-association of the PCy_3 ligand, and hence the active site is more accessible for subsequent addition of monomer units. It may be for this reason that the monomer is consumed faster when the steric bulk in the 7-position is increased.

The amount of initiator consumed at the start of the reaction decreases when the steric bulk of the alkoxy substituent within the monomer is reduced. This is consistent with a decrease in the steric bulk at the 7-position of the monomer enhancing the rate of propagation relative to the rate of initiation compared with a more sterically hindered substituent.

2.3. The effect of the $[M]_o/[I]_o$ ratio on the process of the regeneration of the initiator

The effect of the magnitude of the $[M]_o/[I]_o$ ratio on the regeneration of the initiator for the ROMP of monomers **2a–d** by **1** in $CDCl_3$ has also been studied. Table 2 shows the results of the ROMP reactions performed on these monomers using $[M]_o/[I]_o$=50, 25 and 10.

The process of regeneration observed in these ROMP systems is believed to be in competition with other secondary metathesis reactions such as backbiting, involving internal double bonds along the backbone chains.[18,20] The general trend for the ROMP reactions described in Table 2, shows that as the $[M]_o/[I]_o$ ratio is reduced the extent of regeneration of the initiator decreases. Although the reason for this observation is not fully understood, it could be due to the fact that decreasing the length of the propagating polymer chain leads to an enhancement of the secondary metathesis reactions discussed earlier.

In these systems, the rate of propagation is faster than that of initiation.[20] Therefore, with a lower concentration of monomer in the system, less of the initiator will be

consumed before propagation becomes the dominant process.

2.4. Species X

We have already discussed in detail the observation of regeneration of the initiator at the expense of the propagating living chains when 7-substituted alkoxy norbornadiene monomers are subjected to ROMP initiated by **1**,[17,18] and we now consider the appearance of species X in the alkylidene region of the ^{1}H NMR's. The presence of species X during the ROMP of monomers **2a**–**d** is clearly shown in Figure 6. In all cases species X is stable and long-lived.

When **2d** is subjected to ROMP using **1** with the ratio of $[M]_o/[I]_o=50$, species X is still visible in the ^{1}H NMR spectra one month after the start of the polymerisation, and it is the only observable alkylidene species remaining in solution. The disappearance of the initiator and propagating species is consistent with the known rates of decomposition of ruthenium alkylidene species as reported by Grubbs and co-workers,[21] and it is remarkable that species X still remains in solution after this time. When a second batch of **2d** (18 equiv.) is added to the solution, the monomer is consumed very slowly (20 days), but the appearance of the alkylidene region in ^{1}H NMR remains unchanged i.e. only species X is observed. This observation implies that X is an active metathesis species, which is able to perform ROMP on strained cyclic olefins.

2.5. The effect of the solvent on the regeneration of the initiator

The effect of the solvent on the rate of regeneration of the initiator for the ROMP of **2a** using $[M]_o/[I]_o=50$, has been studied by performing the polymerisations in $CDCl_3$, CD_2Cl_2 and C_6D_6 with $[M]_o/[I]_o=50$ and the results are presented in Table 3. The polarity indices of the solvents according to Allerhand and Schleyer's polarity scale, G, are 106, 100, and 80 respectively.[22] A reduction in the polarity of the solvent has no significant effect on the amount of **1** initially consumed by **2a** or on the extent of regeneration of the initiator, but the overall kinetics for the polymerisation process are retarded (i.e. rate of consumption of the monomer is reduced and the time period over which regeneration was observed is extended). Monomer consumption was fastest in $CDCl_3$ and slowest in C_6D_6. This trend indicates that an increase in the polarity index of the solvent increases the rate at which the ROMP of **2a** occurs. It also reveals that the media in which the polymerisation of **2a** is initiated by **1** plays no role in the regeneration process itself, and that regeneration is solely due to the nature of the monomer and the initiator present.

2.6. ROMP of 5 and/or 6 substituted norbornene monomers

We discussed earlier that norbornadiene monomers with alkoxy functionalities in the 7-position have been found to facilitate the regeneration of initiator **1**. We also showed that the steric bulk of the alkoxy substituent in the monomer unit plays a crucial role in the regeneration process. In order to establish whether the specific position of the alkoxy functionality within the monomer unit has any influence on the process of regeneration of the initiator, monomers with alkoxy groups in the 5 and/or 6 positions of norbornene have been prepared (**6**, **7**, Fig. 4) and subjected to ROMP initiated by **1** in $CDCl_3$. The polymerisations were monitored by ^{1}H NMR spectroscopy in the manner described previously. The alkylidene region of the ^{1}H NMR spectra, shown in Figure 8, indicate that the reactions exhibit similar behaviour to the ROMP reactions of

Table 3. Solvent effects on the ROMP of monomer **2a**[a]

Solvent	Regeneration time (days)	Monomer consumption (h)	Initiator consumption (%)	Extent of regeneration[b] (%)
$CDCl_3$	1.2	1	99	29
CD_2Cl_2	2.5	3.5	97	29
C_6D_6	3	4.5	100	28

[a] Polymerisations were performed at ambient temperature and were initiated by **1** using a ratio of $[M]_o/[I]_o=50$. $[I]_o=15$ mM.
[b] The error associated with the extent of regeneration of the initiator is estimated to be ±5% of the quoted value. The reactions were followed by ^{1}H NMR spectroscopy.

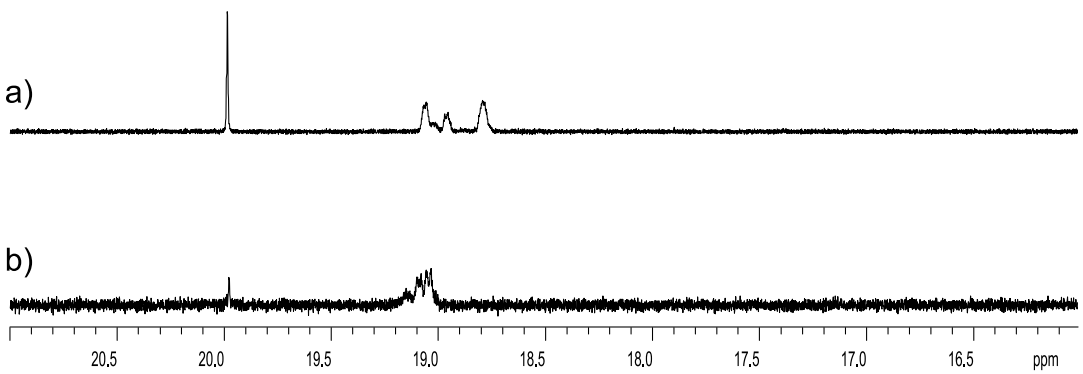

Figure 8. The alkylidene region (21–16 ppm) of the ^{1}H NMR spectra when monomers (a) **6** and (b) **7** are subjected to ROMP by **1** using a ratio of $[M]_o/[I]_o=50$, $[I]_o=15$ mM at ambient temperature.

monomers **3**, **4a**, **4b**, **5a** and **5b** initiated by **1**. There is no regeneration of the initiator, and no species X is observed. This suggests that the specific position of the alkoxy functionality plays a vital role in the regeneration of the initiator and on the formation of species X when alkoxy norbornadiene monomers are subjected to ROMP.

3. Conclusions

The ROMP reactions of 7-alkoxy norbornadiene monomers (**2b**–**d**), using Grubbs well-defined ruthenium initiator showed that as the reaction proceeds the initiator is consumed first and then is partially regenerated at the expense of the propagating species. This is believed to occur by either an intra- or intermolecular secondary metathesis reaction at the living chain ends of the propagating species. A small amount of another carbene species X giving a broad signal at 17.44 ppm, is also formed which is extremely stable in solution. The species X is found to be an active metathesis species and is able to perform ROMP on strained cyclic olefins. The extent of regeneration is found to increase as the steric bulk of the substituent in the 7-position increases.

ROMP of oxygen-containing norbornene monomers without alkoxy groups in the 7-postion (**4a**, **4b**, **5a** and **5b**) and also monomers with alkoxy groups in the 5 and/or 6 positions of norbornene (**6** and **7**) have been performed under similar conditions. None of these systems exhibited regeneration of the initiator and no resonances due to species X can be seen in the ^{1}H NMR spectra. This suggests that the specific position of the alkoxy functionality plays a vital role in the regeneration of the initiator and that it has a pronounced influence on the formation of species X.

A change in the polarity of the solvent has no significant effect on the amount of initiator initially consumed or on the extent of regeneration of the initiator, but the overall kinetics for the polymerisation process are retarded.

It is concluded that regeneration of the initiator and the formation of stable ROMP active alkylidene species is dependent on the position of the alkoxy functionality within the monomer unit. This could be attributed to the ability of the oxygen to coordinate efficiently to the ruthenium metal centre when it is specifically situated in the 7-position of the norbornadiene monomers.

We are currently trying to elucidate the chemical structure of species X and the mechanism by which it performs ROMP. The results of these studies will be published elsewhere.

4. Experimental

4.1. General

All reagents used were of standard reagent grade and purchased from Aldrich or Lancaster and used as supplied unless otherwise stated. THF and $CDCl_3$ (99.9%D, 0.03% v/v TMS) were dried over sodium/benzophenone and P_2O_5, respectively and distilled prior to use. All other solvents were used without prior purification.

Norbornene [**3**] was dried over sodium and distilled under vacuum prior to use. Grubbs ruthenium initiator[6] [**1**], 7-*t*-butoxynorbornadiene[23] [**2a**], 7-methoxynorbornadiene[24] [**2d**], 5-*exo*,6-*endo*-dicarbomethoxynorbornene[25] [**4a**], 5-*exo*,6-*exo*-dicarbomethoxynorbornene[26,27] [**4b**], *exo*,*exo*-N-phenyl-5,6-dicarboxyimidonorbornene[28] [**5a**] and *exo*,*exo*-N-phenylmethyl-5,6-dicarboxyimidonorbornene[28] [**5b**], and *exo*,*exo*-5,6-bis(methoxymethyl)norbornene[29] [**7**] were synthesized according to literature procedures.

^{1}H NMR spectra were recorded on a Varian Mercury 400 or a Varian Inova 500. Chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS), using TMS as the internal reference. ^{13}C NMR were recorded using broad band decoupling on a Varian Mercury 400 or Varian Inova 500 at 100 and 125 MHz, respectively. Electron impact (EI) mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV with the ionisation mode as indicated.

Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser.

4.2. General procedure for ^{1}H NMR scale ROMP reactions

All ROMP reactions were prepared in a Braun glove box under an inert atmosphere. Initiator **1** (10 mg) was dissolved in deuterated solvent (0.4 mL) and stirred for 5 min. The relevant monomer was dissolved in deuterated solvent (0.4 mL). The monomer solution was injected into the initiator solution and stirred for 5 min. The solution was transferred to an NMR tube fitted with a Young's tap, which allowed the vessel to be closed under a nitrogen atmosphere. The reactions were monitored by ^{1}H NMR spectroscopy every 15 min for the first 3 h and then at longer periods until no further reaction was observed. In all cases the integrated intensities of the alkylidene signals were compared to that of the TMS signal, which was assumed to remain constant throughout each experiment.

4.2.1. Preparation of 7-*iso*-propoxynorbornadiene [2b]. Compound **2a** (6.94 g, 42.3 mmol) was dissolved in propan-2-ol (50 mL) under an inert atmosphere and sulphuric acid (7 mL) dissolved in propan-2-ol (50 mL) was added dropwise with stirring. The solution was heated to 40 °C and stirred for 3 days. The reaction mixture was poured onto ice (75 g) and extracted with dichloromethane (3×25 mL). The combined organic layers were washed successively with saturated solutions of $NaHCO_3$ (3×50 mL) and NaCl (3×50 mL). After drying over $MgSO_4$ and filtering, the solvent was removed under vacuum and the residue was purified by fractional distillation under reduced pressure to afford 2.68 g (52–54 °C/18 mbar) of **2b** (yield 42.3%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (t, 2H, J=2.4 Hz), 6.56 (t, 2H, J=1.6 Hz), 3.70 (s, 1H), 3.51 (m, 1H, J=6.4 Hz), 3.48 (m, 2H, J=2.0 Hz), 1.10 (d, 6H, J=6.4 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 137.4, 108.0, 70.4, 54.1, 22.7 ppm. Anal. calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39.

Found: C, 79.79; H, 9.33. MS (EI): m/z=149.0 $[M-H]^+$, 135.0 $[M-CH_3]^+$, 106.9 $[M-CH(CH_3)_2]^+$, 91.2 $[M-OCH(CH_3)_2]^+$.

4.2.2. Preparation of 7-ethoxynorbornadiene [2c]. Compound **2a** (20.6 g, 0.125 mol) was dissolved in ethanol (200 mL) under an inert atmosphere and sulphuric acid (14 mL) was added dropwise. The solution was heated to 30 °C and stirred for 5 h. The reaction mixture was poured onto ice (150 g) and extracted with dichloromethane (4×25 mL). The combined organic layers were washed successively with saturated solutions of $NaHCO_3$ (3×50 mL) and NaCl (3×50 mL). After drying over $MgSO_4$ and filtering, the solvent was removed under vacuum and the residue was purified by fractional distillation under reduced pressure to afford 2.75 g (48–50 °C/18 mbar) of **2c** (yield 16.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (m, 2H, J=1.2 Hz), 6.57 (m, 2H, J=1.2 Hz), 3.65 (m, 1H, J=0.8 Hz), 3.52 (m, 2H, J=2.0 Hz), 3.37 (q, 2H, J=7.2 Hz), 1.13 (t, 3H, J=7.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 137.3, 109.1, 64.0, 53.1, 28.5, 15.4 ppm. Anal. calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.21; H, 8.63. MS (EI): m/z=136.0 $[M]^+$, 106.9 $[M-CH_2CH_3]^+$, 91.3 $[M-OCH_2CH_3]^+$.

4.2.3. Preparation of *exo*-5-methoxymethylnorbornene [6]. Under an inert atmosphere, *exo*-5-methanolnorbornene (3.20 g, 25.8 mmol) dissolved in dry THF (10 mL) was added dropwise to a stirred solution of NaH (0.77 g, 32.2 mmol) in dry THF (30 mL). After complete addition, the solution was stirred for 30 min. Methyl iodide (9.14 g, 64.4 mmol) was added dropwise to the solution and a slight exotherm was observed. The reaction was stirred at room temperature for 2 h. Water (~5 mL) was added dropwise to quench any remaining NaH. The solution was poured onto ether (250 mL) and filtered. It was then washed with water (4×100 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under vacuum to yield the crude product (3.88 g) as a yellow oil. The residue was purified by fractional distillation under reduced pressure to afford 1.81 g (68–72 °C/45 mbar) of **6** (yield 50.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10 (dd, 1H, J=5.6, 2.8 Hz), 6.05 (dd, 1H, J=5.6, 2.8 Hz) 3.42 (dd, 1H, J=9.2, 6.4 Hz), 3.36 (s, 3H), 3.29 (t, 1H, J=8.8 Hz), 2.80 (br. s, 1H), 2.73 (br. s, 1H), 1.68 (m, 1H), 1.31 (q, 2H, J=4.4 Hz), 1.24 (dt, 1H, J=11.6, 2.0 Hz), 1.11 (dt, 1H, J=11.6, 4.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8 (2), 136.8 (0), 77.8, 59.0, 45.2, 43.9, 41.7, 39.1, 29.9 ppm. Anal. calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.83; H, 10.04. MS (EI): m/z=138.0 $[M]^+$, 123.0 $[M-CH_3]^+$, 107.0 $[M-OCH_3]^+$, 90.9 $[M-CH_2OCH_3]^+$.

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